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THE EFFECT OF CERTAIN ADDITIVES ON CRITICAL DIAMETER AND COMBUSTION RATES OF MIXTURES OF ALUMINUM WITH GELLED WATER

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7 January 1974

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TRANSLATION

In Reply Refer to:
FSTC-HT-23-1509-73
DIA Task No. T70-23-01

Date: 7 January 1974

ADA000210

ENGLISH TITLE: The Effect of Certain Additives on Critical Diameter and Combustion Rates of Mixtures of Aluminum with Gelled Water

SOURCE: Izv. vyssh. ucheb. zaved. khim. I Khim, tekhnol. 13 (3), 1970, pp. 318-321.

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LANGUAGE: Russian

COUNTRY: USSR

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ABSTRACT: Critical diameter and combustion rate at atmospheric pressure, combustion rate vs. pressure in the 20-100 atm range, and completeness of oxidation of aluminum at pressures of up to 60-100 atm were determined for 50:50 $Al:H_2O$ and stoichiometric $Mg:H_2O$ mixtures, with and without addition of 1-5% KF, NaF, LiF, AlF_3 and NaOH. Graphs of the resulting data are presented. It is concluded that these additives increase $Al + H_2O$ ignitibility and decrease critical diameter, that NaF and KF have a greater effect on combustion rate than the others and that the improved ignition and combustion result from the action of boiling water solutions of NaF and KF in destruction of the oxide films.

NOTICE

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It is well known that ignition and combustion of aluminum powder is significantly impaired by the presence of a solid and high melting film of oxide on the surface of particles of it [1,2]. By disrupting the integrity of this film, by means of some physical or chemical actions, its protective properties can be decreased and the ignition and combustion of aluminum can be facilitated in this manner. One of the possible means is reduction of the melting temperature of the oxide film by introduction of the fluorides of metals, which form low melting complex compounds with Al_2O_3. The significant decrease in flash point of a mixture of $KClO_4$ with aluminum by addition of aluminum fluoride can be pointed out as an example [3].

The effect of Li, Na, K and Al fluorides on the critical diameter and combustion rate of a mixture of aluminum powder with water was investigated in this work [4,5].

A sample of water, gelated with 3% sodium salt of carboxymethylcellulose (CMC), was thoroughly mixed with aluminum powder (mean aluminum particle size, 1 μ, was determined in a PSKh-2 instrument), the quantity of which corresponded to the stoichiometric composition $Al:H_2O=50:50$. In introduction of the additive, a sample of fluoride was mixed with aluminum powder beforehand. The slightly soluble Li and Al fluorides had particle sizes of less than 50 μ. The soft mixture was rubbed through a 160 μ mesh screen with a rubber stopper, to obtain small granules, a sample of which was placed in a small glass beaker and compressed manually to a density of 1.0-1.1 g/cm^3 (K_{pack} = 0.5-0.6).

The charge was ignited with a nichrome spiral, heated by an electric current, and sometimes with an intermediate charge, for which a mixture usually was used which was close to the one being studied in composition and igniting easily under the test conditions.

The experiment consisted of three sections: a) determination of the critical diameter (d_{cr}) and combustion rate at atmospheric pressure (in air); the combustion time was measured with a stop watch in this case; the length of the section of charge on which the measurement was made was 15-20 mm; b) determination of relation of combustion rate to pressure in the 20-100 atm range, in a constant pressure bomb in a nitrogen atmosphere; a photo recorder was used for combustion rate measurements; c) determination of completeness of oxidation of aluminum by burning the mixture in a manometric bomb under increasing pressure, up to 60-100 atm; the volume of hydrogen liberated by burning of the charge was measured.

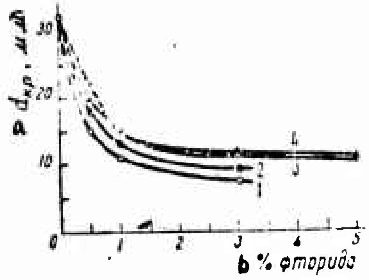

Fig.1: Effect of metal fluoride additives on critical diameter of combustion of $Al:H_2O=50:50$ mixture; ($\rho = 1.0$ g/cm^3, H_2O+3% CMC, mean Al particle size 1μ); Additives: 1 - KF, 2 - NaF, 3 - LiF, 4 - AlF_3; (points on curves are smallest diameters of charge at which combustion was observed).

Key: a. d_{cr}, mm b. % fluoride

The results of the experiment on the effect of metal fluorides on d_{cr} of the $Al:H_2O=50:50$ mixture are shown in Fig. 1. The greatest reduction in d_{cr} takes place in the case of addition of the highly water-soluble Na and K fluorides, and introduction of the slightly soluble Li and Al fluorides affected the value of d_{cr} less. Introduction of the additives was almost not reflected at all in the combustion rates; in all cases, it was 0.15-0.18 cm/sec.

Sodium hydroxide also was tested as an additive to the $Al+H_2O$ mixture. Water solutions of it were prepared with concentrations of 0.04%, 0.4% and 0.8%, having a pH of 12.0, 13.0 and 13.2, respectively.

The tests showed that replacement of water by alkali solutions leads to considerable decrease in d_{cr}: with a 0.04% NaOH content, a decrease in d_{cr}

from 32 to 15 mm takes place. With increase in NaOH content, some decrease in d_{cr} still takes place, to 13.0 and 12.8 mm, respectively.

Introduction of 5% KCl into the mixture, not only does not decrease, but even somewhat increases (from 32 to 37 mm) the critical diameter; the $Al+H_2O$ mixture with KCl burns very slowly and irregularly.

For the purpose of testing whether or not the effect of fluorides is specific only for aluminum mixtures, we tested addition of LiF to a $Mg:H_2O=57:43$ mixture. The experiment showed that the mixture without additive burns at a diameter of 12 mm, and introduction of 5% LiF increases d_{cr} to 18 mm. Mixtures with and without fluoride additive burn very irregularly.

To determine the relation of combustion rate to pressure, charges with metal fluoride additives, in the amount of 1% of the weight of aluminum, were used.[1] Charge density was 1.0-1.1 g/cm^3.

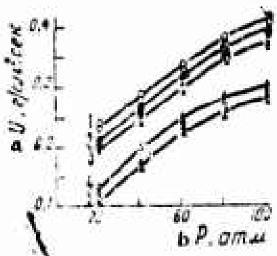

Fig.2: Combustion rate vs. pressure for $Al:H_2O=$ 50:50+1% metal fluoride mixture (ρ=1.0-1.1 g/cm^3; H_2O-3% CMC; Al particle size 1 μ); additives: 1 - NaF, 2 - KF, 3 - LiF. 4 - without additive, 5 - AlF_3.

Key: a. U, $g/cm^2 \cdot$ sec b. P, atm for atmosphere

As is evident from Fig.2, the combustion rate increases with increase in pressure; the curves have a weakly expressed saturated nature. The addition of 1% alkali metal fluorides (Na, K, Li) increases the combustion rate by a factor of about 1.5, not significantly changing the nature of the relation of rate to pressure. Addition of 1% AlF_3 not only does not accelerate, but even retards the combustion process.

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[1]With the example of LiF, it was determined that increase in fluoride content in the mixture does not show up in the combustion rate and the nature of its relation to pressure. The U=f(P) curve for $(Al+H_2O)_{stoi}$+5%LiF mixture practically coincides with the curve for a mixture containing 1% LiF.

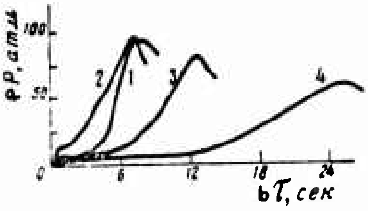

Fig.3: Manometric P-τ curves of combustion of $Al:H_2O=50:50$ mixture with addition of 1% metal fluorides; additives: 1 - NaF, 2 - Kf, 3 = LiF, 4 - AlF_3.

Key: a. P, atm b. τ, sec

The completeness of oxidation of the metal was determined in a manometric bomb. A 20-22 mm diameter charge, having a density of 0.45-0.55 g/cm^3 (K_{pack}= 0.2-0.3) was burned. A stoichiometric mixture of Mg + BaO_2, in the amount of 2 g, was used as the igniter. Efforts were made to ignite the $(Al+H_2O)_{stoi}$ mixture without additive, under the same conditions. It was very difficult to ignite the mixture, and combustion was achieved in only two tests. In this case, the mixture was not rubbed through the screen, but was broken up right in the small glass beaker serving as the charge casing. The tests showed that completeness of oxidation of aluminum amounted to only 44-53% in burning of the $(Al+H_2O)_{stoi}$ mixture without additive. Introduction of Li, Na, K and Al fluorides into the mixture increases the completeness of oxidation of aluminum to 68-74%. The manometric P-τ curves, obtained by burning the $Al+H_2O$ mixture with 1% fluoride additives, are shown in Fig. 3. Despite the considerable pressures reached (60-100 atm), combustion was slow and the total combustion time was from 7 to 25 seconds. The mixtures with NaF and KF burned faster than the others (7 seconds), a slower combustion rate was observed with addition of LiF (13 seconds), and the combustion process of the mixture with AlF_3 additive extended to 25 seconds, with the pressure increasing only to 60 atm.

Attempts to intensify the combustion of the $(Al+H_2O)_{stoi}$ mixture in the manometric bomb by adding 5% NaCl to it were unsuccessful; we did not succeed in igniting this mixture. A test of the $(Mg+H_2O)_{stoi}$ mixture, with 10% LiF additive, in the manometric bomb, showed that lithium fluoride does not intensify combustion of the water-magnesium mixture under conditions of increased pressure; neither the time, maximum pressure, nor completeness of oxidation of the magnesium changed significantly. We note in conclusion that we did not carry out burning tests of $Al+H_2O$ mixtures containing more than 3% Na and K fluorides, since these mixtures proved to be chemically unstable: 10-15 minutes after preparation of mixtures containing 5% NaF or KF, they began to heat up strongly and complete boiling off of the water from the mixture took place. It should be assumed that, together with reversible hydrolysis of the fluorides $2NaF+H_2O \rightleftharpoons NaHF_2+NaOH$, the process of destruction of the oxide film on the aluminum took place, i.e.,

$$Al_2O_3 + 12NaF_{aq} + 3H_2O = 2Na_3AlF_6 + 6NaOH + 10 \text{ kcal},$$ [1]

and the alkali medium caused energetic oxidation of the exposed metallic aluminum after removal of the oxide film.

Determination of the pH of water solutions of sodium and potassium fluorides (by means of a LPU-01 potentiometer) gave values of 8.7 and 8.0, respectively. The pH of suspensions of $Al(OH)_3$ in water, which we prepared, proved to be 7.5. Addition of fluoride water solutions to this suspension considerably increased the alkalinity of the system. Measurement of the pH gave the following results: $Al(OH)_3+NaF_{aq}$, 11.4; $Al(OH)_3+KF_{aq}$, 10.8. LiF solution had pH of 8.8 and, after mixing with the $Al(OH)_3$ suspension, 9.4. A suspension of AlF_3 separately had a pH of 6.9 and, after combination with the $Al(OH)_3$ suspension, 7.7.

These tests confirm the reaction equations which we presented above, for the case of sodium (potassium) fluorides and, to a lesser extent, lithium fluoride. Aluminum fluoride and $Al(OH)_3$ obviously do not react together, and a noticeable pH change was not observed in this case.

Finally, we prepared a 0.1 M water solution of NaOH, having a pH of 13, and a $Al+H_2O(NaOH)$ mixture was prepared using it; the gelling agent (CMC) was not used in this case, since the Al powder is wetted well by the alkali solution. This mixture ignited and burned in the manometric bomb in 5-6 seconds, creating a pressure of 115-130 atm. The completeness of oxidation of the aluminum in this case was 73-74%.

Conclusions

1. It was shown that addition of 1-5% Li, Na, K and Al fluorides to a standard $(Al+H_2O)_{stoi}$ mixture increases its ignitibility and decreases the critical diameter of combustion at atmospheric pressure. The highly water-soluble sodium and potassium fluorides showed a greater effect on ignition and combustion processes of the mixture than the slightly water-soluble lithium and aluminum fluorides.

2. A considerable increase in pH of water solutions of NaF and KF, upon addition of an $Al(OH)_3$ suspension to them, permits it to be proposed that the abovementioned phenomena during combustion should be explained by intensive decomposition of the oxide film on the aluminum particles by the action of the boiling water solutions of sodium and potassium fluorides on them.

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[1] The value $\Delta H_{298} = -784.8$ kcal/mole was used for Na_3AlF_6 in the calculation [6].

BIBLIOGRAPHY

1. Shidlovskiy, A.A., Osnovy pirotekhniki [Foundations of Pyrotechnics], Mashinostroyeniye Press, Moscow, 1964.

2. Mellor, A. M. and J. Glassman, Pyrodynamics, 3, 1965, p. 43.

3. Freeman, E. S. and D. A. Anderson, Comb. and Flame, 10, 1966, p. 337.

4. Shidlovskiy, A. A., Dokl. AN SSSR, 51, 1946, p. 127.

5. Gorbunov, V. V., A. V. Vasil'yev and A. A. Shidlovskiy, Izv. VUZ SSSR khimiya i khim. tekhnologiya, 12, 1969, p. 1171.

6. Goughlin, I. P., J. Amer. Chem. Soc., 80, 1958, p. 1802.